R56-22

Reprinted from SCIENCE, June 8, 1956, Vol. 123, No. 3206, pages 1038–1039.

New Synthesis of Oxalic Acid

Results indicate that oxalic acid is formed when bicarbonates in aqueous solutions are exposed to beta or gamma radiation. Although the procedure appears less complicated than Wöhler's synthesis of this acid from cyanogen, which was the first "organic" synthesis from "inorganic" materials (*1*), the mechanism of the reaction is complex, since it involves the presence of water and possibly also oxygen to effect the carbon to carbon bondage of the carbon dioxide moiety.

Solutions of ammonium, calcium, and sodium bicarbonates and sodium and ammonium carbonates were prepared in various concentrations and irradiated in polyethylene bags. In order to allow complete penetration of the ionizing radiation, a large enough bag was used so that the thickness of the filled bag (approximately 250 ml) was nowhere greater than 6 mm. The samples were exposed to beta radiation by means of a 2 Mev van de Graaff electron accelerator. The dose rate was 2.10 Mrep per pass, and the total dosages to which the samples were exposed ranged from 2.10 to 52.5 Mrep.

The chemicals used were of standard analytic grade. Calcium bicarbonate was prepared by passing carbon dioxide through a water suspension of calcium carbonate. The samples, which were irradiated at room temperature, were withdrawn from the polyethylene bags, and the oxalic acid, which was precipitated as calcium oxalate, was regenerated and derivatized. Table 1 gives the characterization of oxalic acid for all series investigated.

These results were repeated when glass vials were used as containers. Owing to the porosity of the polyethylene bags, gas analyses were not attempted.

Oxalic acid was not detected on irradiation of sodium carbonate solutions. Blank tests, carried out with distilled water, were also negative. Formic acid

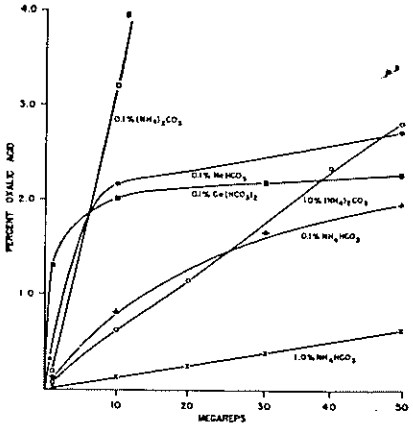

Fig. 1. Oxalic acid yield versus irradiation dose.

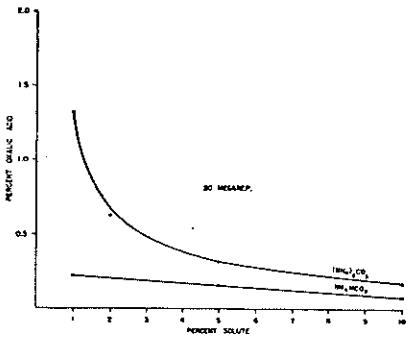

Fig. 2. Oxalic acid yield versus concentration of solution.

was likewise not observed to form in these reactions. The formation of oxalic acid from ammonium carbonate is explained by the fact that ammonium carbonate is a mixture of ammonium bicarbonate, ammonium carbamate, and ammonia (*2*).

Percentage yields of oxalic acid were calculated as 100 times the number of grams of oxalic acid formed per gram of solute. G values (number of molecules formed per 100 ev where 52.4×10^{18} ev is equivalent to 1 Mrep) may be obtained by simple calculations from values in Figs. 1 and 2.

Table 1. Identification of oxalic acid.

Test	Theoretical	Found
Neutralization equivalent CHO · 2HO	63	62.5 ± 1.0
Oxalic acid dihydrate, mp °C	100* (*1*)	100 ± 0.2
Oxalic acid, mp °C	189.5* (*3*)	190 ± 0.2
Benzylthiuronium oxalate, mp °C	193* (*4*)	193 ± 0.2
Aniline blue formation (*5*)	+	+
Infrared spectrum of calcium oxalate†		

* Mixed melting points with authentic materials showed no depression. (All melting points were carried out on Kohfler hot stage.)
† Spectrum agreed with standard calcium oxalate curve.

It was qualitatively determined that gamma irradiation at similar dosages also results in the formation of oxalates from the afore-mentioned bicarbonates and ammonium carbonate.

The yields of oxalic acid, obtained by permanganate oxidation, for varying concentration and dosage levels are presented in Figs. 1 and 2, respectively.

TORSTEN HASSELSTROM
MALCOLM C. HENRY
Quartermaster Research and Development Command, Pioneering Research Division, Natick, Massachusetts

References and Notes

1. E. Hjelt, *Geschichte der Org. Chemie* (Braunschweig, 1915), p. 38.
2. J. J. R. MacLeod and H. D. Haskins, *J. Biol. Chem.* 1, 319 (1905).
3. E. Bamberger and H. Althausse, *Ber. deut. chem. Ges.* 21, 1901 (1888).
4. J. J. Donleavey, *J. Am. Chem. Soc.* 58, 1804 (1936).
5. F. Feigl, and O. Frehden, *Mikrochemie* 18, 272 (1935).

5 December 1955